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MINERALS FROM MACEDONIA

VI. SEPARATION AND IDENTIFICATION OF SOME SULFIDE MINERALS

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Abstract: Among the rich ore deposits present in Macedonia, the sulfide minerals are being the mostly exploited ones. Some of these minerals appear as well formed single crystal species in the nature, but often some other mineral forms accompany them. The difficulties connected with the selection, separation, purification, identification and characterization of several sulfide minerals (galena, PbS; sphalerite/wurtzite (Zn,Fe)S; pyrite, FeS_2; chalcopyrite, $CuFeS_2$) from various localities (Sasa, Bučim, Zletovo, Toranica) were discussed. Identification was based on the comparison of our results (obtained by use of the infrared and Raman vibrational spectroscopy and powder X-ray diffraction) with the corresponding literature data for the analogous mineral species originating all over the world.

Key words: sulfide minerals; galena; sphalerite/wurtzite; pyrite; chalcopyrite; Macedonia; FTIR and Raman spectroscopy, powder X-ray diffraction

INTRODUCTION

Sulfide minerals from Allchar mine deposit in Macedonia have been intensively studied during the last decade using vibrational (infrared and Raman) spectroscopy (Trajkovska *et al.*, 1992; Trajkovska *et al.*, 1993; Šoptrajanov *et al.*, 1993; Šoptrajanov *et al.*, 1994a; Šoptrajanov *et al.*, 1994b). Recently, a systematic study has been undertaken in order to collect, select, identify, characterize and systematize all minerals originating from Macedonia.

Although separation of minerals is, in general, simple process, sometimes it requires much time and patient work. Especially troublesome, problematic and delicate for purification are the small grained minerals, appearing in aggregates of many mineral samples, as it is for example, the case with pyrite and chalcopyrite. The separation of mineral specimens from the impurities however mostly depends on the crumbled monocrystals as well as the quantity of present ore impurities.

In this work, the results of the study and identification of some of the collected sulfide minerals [galena, PbS; pyrite, FeS_2; chalcopyrite, $CuFeS_2$ and sphalerite/wurtzite, (Zn,Fe)S], using FTIR and Raman spectroscopy as well as powder X-ray diffraction methods are presented. Identification was based on the comparison of the results of our study with the literature data for the corresponding mineral species originating from other localities all over the world. Some of the difficulties that appeared along the process of the selection, purification and identification are also discussed.

EXPERIMENTAL

Monocrystals were picked up under a microscope from the ore samples. The mineral samples were collected from various localities in Macedonia: Sasa (galena, pyrite, sphalerite/wurtzite),

Zletovo (galena, chalcopyrite), Bučim (pyrite, chalcopyrite) and Toranica (sphalerite/wurtzite).

The far infrared spectra of the studied samples were recorded on a Bruker 113v FTIR interferometer using mulls in Nujol between polyethylene plates. Jobin Yvon LabRam Infinity spectrometer with 532 nm laser line of an Nd-YAG frequency-double laser was used for recording the presented Raman spectra.

The GRAMS ANALYST 2000 package (1991–1993) was involved in analyzing the spectra while GRAMS32 package (1991–1996) helped in treatment of the recorded spectra.

Philips Analytical X-ray Diffractometer PW3710 was used for X-ray powder diffraction. Generator with 50 kV and electricity of 30 mA were employed as a source for Cu$K\alpha$ radiation.

RESULTS AND DISCUSSION

Galena

Four galena samples (two from Sasa and two from Zletovo deposits) were studied. The appearance of only one extremely wide, intense and complex band in the infrared spectrum of the studied samples whose maximum, depending from sample to sample, ranges from 155–164 cm^{-1} (Fig. 1), is in agreement with the corresponding data found in the literature. Namely, a unique band has been registered in the same spectral region in the infrared spectrum of galena samples studied by (Farmer, 1974; Soong and Farmer, 1978; Плюснина, 1977). Exception is the second band mentioned by Плюснина (1977) at 70 cm^{-1}. The more detailed analysis of the studied spectra of the four samples of galena shows that this band appears as a shoulder on the low-frequency side of the mentioned complex band. The weak and not well-defined band in the spectra of the studied samples around 365 cm^{-1} (Fig. 1), probably originates from the present impurities in the studied samples.

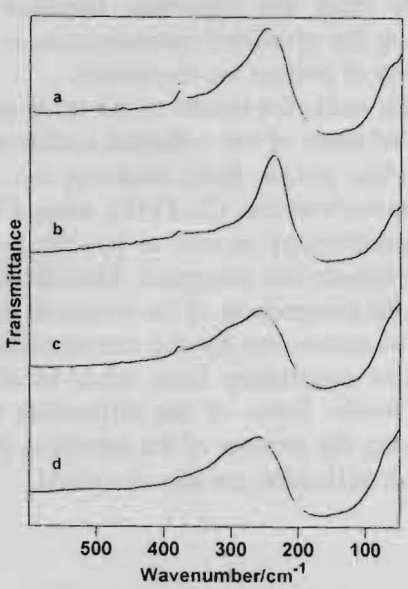

Fig. 1. The FTIR spectra of galena from Zletovo (a, d) and Sasa (b, c)

Raman spectra of four galena samples shown in Fig. 2 are very similar to each other suggesting that they belong to the same mineral sample. According to group theory (Soong and Farmer, 1978), no first-order Raman spectrum is expected in galena, which is confirmed from the Raman spectra on Fig. 2. A broad and weak band at around 265 cm^{-1} is detected in all samples. The fact that its intensity varies from sample to sample could be an indication of the presence of some impurities in the studied samples of galena. On the other hand, a weak band at around 960 cm^{-1}, which appears in the Raman spectra of all studied galena samples with more or less the same intensity, could be regarded as an indication about the possible presence of SO_4^{2-} groups.

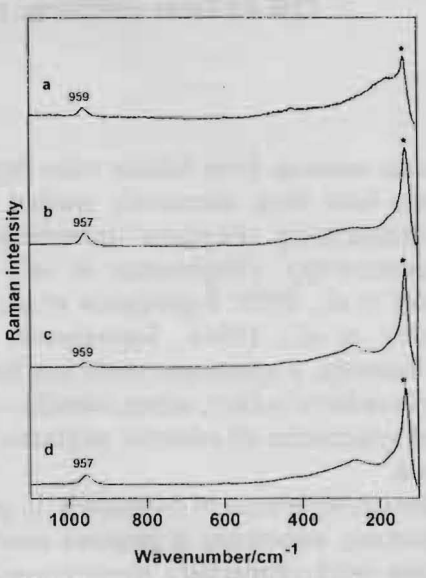

Fig. 2. The Raman spectra of galena from Zletovo (a, b) and Sasa (c, d) (* – "filter cut-out" from the Rayleigh line)

The great similarity between the powder X-ray diagrams of the studied galena samples from Sasa and Zletovo shown on Fig. 3 could be taken as an additional evidence that the studied samples belong to the same mineral. Their identity is

proved by the comparison of the *d* values of the eight most intense maxima in the diagrams of the two studied samples (from Zletovo and Sasa), with the corresponding maxima for the galena mineral sample taken from the literature (Berry, 1972) (Table 1). As seen from Table 1, the eight most intense maxima in the X-ray powder diagrams of the studied mineral samples are accompanied with the practically same *d* values found in the galena X-ray diagram (Berry, 1972).

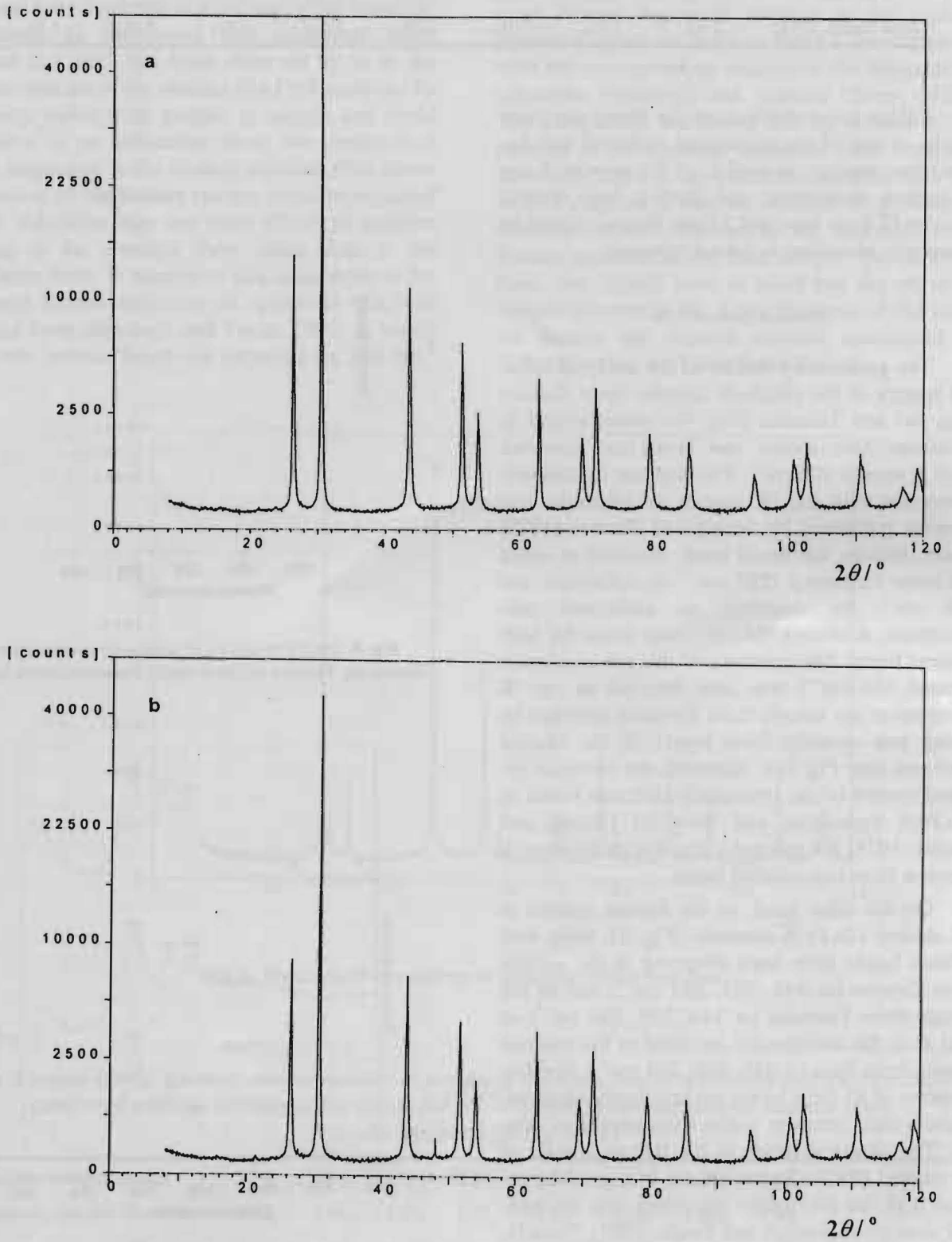

Fig. 3. The powder X-ray diagrams of galena from Sasa (a) and Zletovo (b)

Table 1

The d *values for the eight most intense maxima in powder X-ray diagrams of galena from Zletovo and Sasa compared to the corresponding diagram for the galena taken from the literature (Berry, 1972)*

Galena (Zletovo)	2.92_x	3.36_2	2.08_2	1.77_2	1.32_1	1.70_1	1.47_1	1.35_1
Galena (Sasa)	2.93_x	3.38_3	2.08_3	1.78_2	1.32_1	1.70_1	1.48_1	1.36_1
Galena (Berry, 1972)	2.97_x	3.43_8	2.10_6	1.79_4	1.33_2	1.71_2	1.48_1	1.36_1

Taking into consideration the above discussed results of use of the vibrational (infrared and Raman) spectroscopy as well as of the powder X-ray diffraction techniques, the studied four mineral samples (2 from Sasa and 2 from Zletovo) could be univocally identified as galena minerals.

Sphalerite/wurtzite

The preliminary results of the study of infrared spectra of the (Zn,Fe)S samples from Zletovo (Fig. 4a) and Toranica (Fig. 4b) contemplated as sphalerite have shown one broad and complex band at around 300 cm^{-1}. This was not in complete agreement with the IR spectra of sphalerite and wurtzite published by Soong and Farmer (1978) where, besides the broad band observed at about the same frequency (297 cm^{-1} for sphalerite and 299 cm^{-1} for wurtzite), an additional sub-maximum, at around 334 cm^{-1}, was found for both mineral forms. The existence of this sub-maximum (around 334 cm^{-1}) was later detected in our IR spectrum of the sample from Toranica recorded by taking less quantity (thin layer) of the studied specimen (see Fig 4c). However, the identical infrared spectra of the structurally different forms of (Zn,Fe)S (sphalerite and wurtzite) (Soong and Farmer, 1978) did not make possible to distinguish between these two mineral forms.

On the other hand, in the Raman spectra of the studied (Zn,Fe)S minerals (Fig. 5), three well defined bands have been observed in the sample from Zletovo (at 345, 323, 293 cm^{-1}) and in the sample from Toranica (at 344, 323, 296 cm^{-1}) as well as in the additionally included in the analysis sample from Sasa (at 345, 324, 294 cm^{-1}). The frequencies of all three bands are practically identical, whereas their intensity varies from sample to sample. The observed bands in the Raman spectra of the studied (Zn,Fe)S samples are in a good agreement with the previously published data for mineral wurtzite (Mernagh and Trudu, 1993). Namely, the above mentioned three bands observed in the

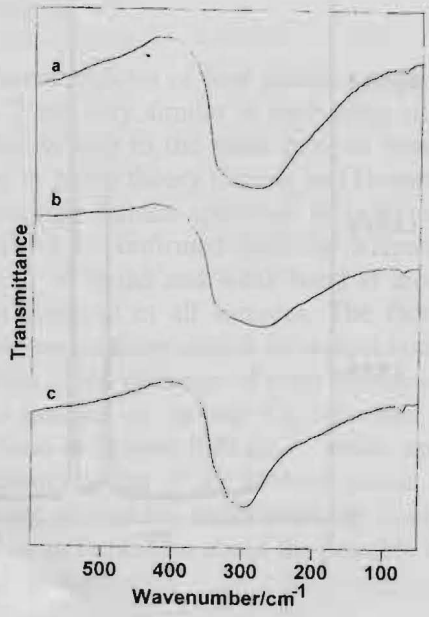

Fig. 4. The FTIR spectra of sphalerite/wurtzite from Zletovo (a), Toranica (b) (thick layer), Toranica (c) (thin layer)

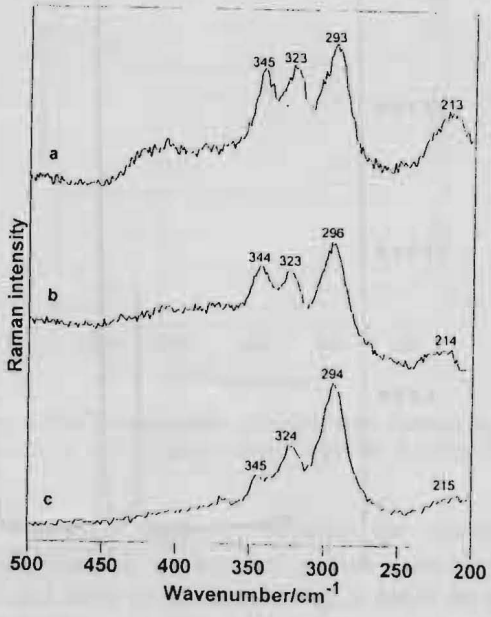

Fig. 5. The Raman spectra of sphalerite/wurtzite from Zletovo (a), Toranica (b) and Sasa (c)

spectra of Zletovo, Toranica and Sasa samples have their equivalencies in the most intense bands (at 350, 327 and 297 cm^{-1}) in the wurtzite spectrum recorded and discussed by Mernagh and Trudu (1993). The rest of the bands (in the spectral region 500 – 200 cm^{-1}), mentioned by these two authors, were reported to have negligible intensity. It should be mentioned that additional band, around 214 cm^{-1}, has been observed by us in the Raman spectra of the studied (Zn,Fe)S samples. Its intensity varies from sample to sample and could be taken as an indication about the presence of some impurities in the studied minerals. The above discussion of the Raman spectra could be regarded as an indication that our three (Zn,Fe)S samples belong to the wurtzite form rather than to the sphalerite form. In support to this assumption is the reported Raman spectrum of sphalerite (Zn,Fe)S mineral form (Mernagh and Trudu, 1993) in which only two intense bands are expected (at 350 cm^{-1} for the LO mode and at 275 cm^{-1} for the TO mode).

The X-ray powder diffraction diagram of the (Zn,Fe)S sample from Sasa deposit was only recorded (Fig. 6). For the purpose of the further identification of the studied (Zn,Fe)S mineral form, ten most intense registered maxima in the studied powder diagram are listed in Table 2 and compared with the corresponding maxima in the diagrams of sphalerite (synthetic) and wurtzite (Berry, 1972). The comparison has shown that the powder X-ray patterns of the synthetic sphalerite taken from the literature (Table 2) are practicaly identical with the studied diagram. It does not confirm the previously discussed results obtained by the analysis of the Raman spectrum of the Sasa sample. On the other hand, one should have in mind that the six most intense maxima in the X-ray diagrams of the studied sample and mineral wurtzite correspond to each other very well (see Table 2).

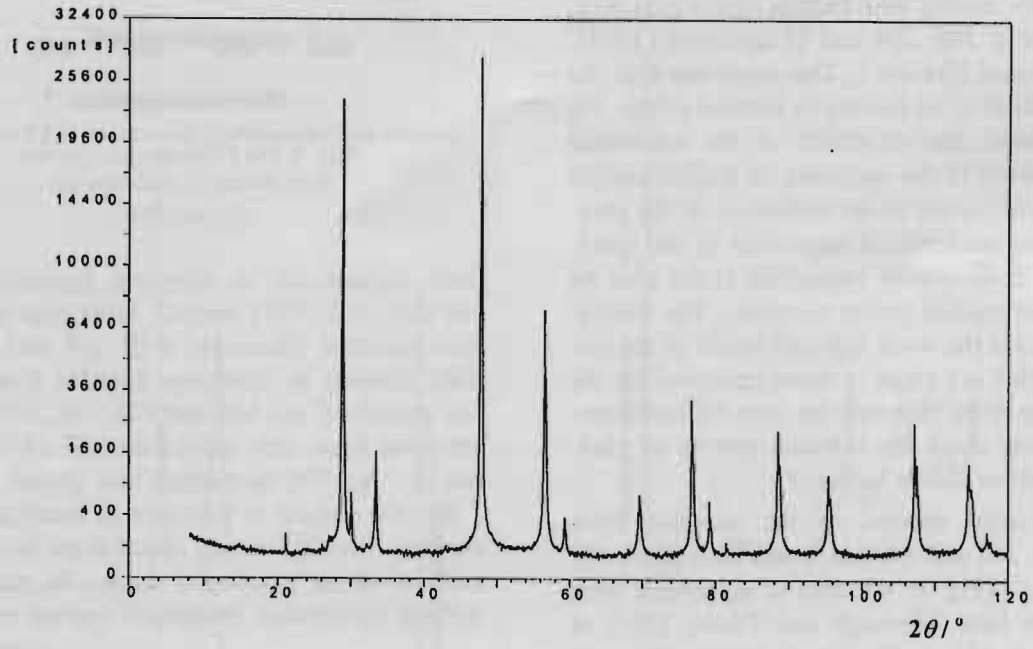

Fig. 6. The powder X-ray diagram of sphalerite/wurtzite from Sasa

Table 2

The d values for the ten most intense maxima in powder X-ray diagrams of sphalerite/wurtzite from Sasa compared with the corresponding values for synthetic sphalerite and mineral wurtzite taken from the literature (Berry, 1972)

Sphalerite/wurtzite (Sasa)	3.10_8	1.91_x	1.63_3	2.69_1	1.24_1	1.10_1	1.35_1	1.04_1	2.97_1	0.91_1
Sphalerite, syn (Berry, 1972)	3.12_x	1.91_5	1.63_3	2.71_1	1.24_1	1.10_1	1.35_1	1.04_1		
Wurtzite (Berry, 1972)	3.12_x	1.90_5	1.63_4			1.10_1			2.93_1	0.91_1

One could therefore conclude that the application of three the most frequently used instrumental techniques (infrared and Raman vibrational spectroscopy and powder X-ray diffraction) for mineral identification and characterization does not necessarily and unequivocally enable the distinction between the mineral forms which often appear together and undergo transformation from one to the other form (Bermanec, 1999).

Pyrite

The infrared spectra of the two studied pyrite samples from Bučim and Sasa (see Fig. 7) show three bands with the following frequencies: 412, 347, 290 cm^{-1}. Six additional weak bands (below 250 cm^{-1}) are present in the spectrum of the Bučim sample. Our data are in good agreement with those reported in literature for mineral pyrite. Thus, three spectral bands with almost the same frequencies were reported by Farmer (1974): at 415, 348 and 293 cm^{-1}; by Soong and Farmer (1978): at 416, 400 (shoulder), 349, 294 and Плюснина (1977): at 422, 349 and 294 cm^{-1}. This confirms that the samples studied by us belong to mineral pyrite. On the other hand, the existence of the additional bands registered in the spectrum of Bučim sample below 250 cm^{-1} could be an indication of the presence of some unidentified impurities in the specimen. Some chalcopyrite impurities could also be present in all studied pyrite samples. The indication for this are the weak infrared bands at the frequencies which are close to those expected for the bands arising from chalcopyrite (see the forthcoming discussion about the infrared spectra of chalcopyrite samples shown in Fig. 9).

The Raman spectra of the samples from Bučim (425, 375 and 340 cm^{-1}) and Sasa (427, 378 and 341 cm^{-1}) (Fig. 8) are also in agreement with the literature data (Mernagh and Trudu, 1993: at 428, 377 and 342 cm^{-1}). Three additional bands however are present in the Raman spectrum of Sasa pyrite sample at 406, 290 and 224 cm^{-1}. At least one of them (290 cm^{-1}) indicates that impurities of chalcopyrite are present in the studied specimen.

The indications obtained by the vibrational (infrared and Raman) spectroscopy undoubtedly implicates that the above studied samples belong to the mineral pyrite. This should be, however, additionally confirmed by the study of their powder X-ray diffraction patterns.

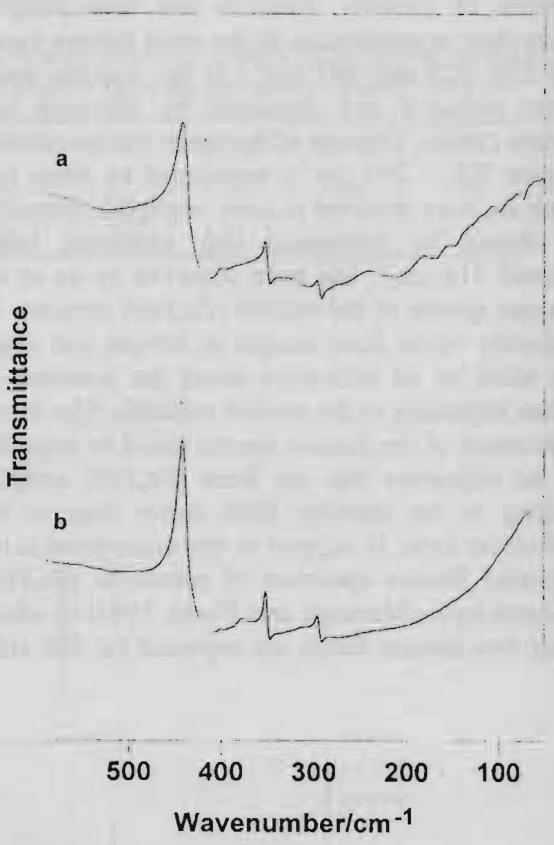

Fig. 7. The FTIR spectra of pyrite from Bučim (a) and Sasa (b).

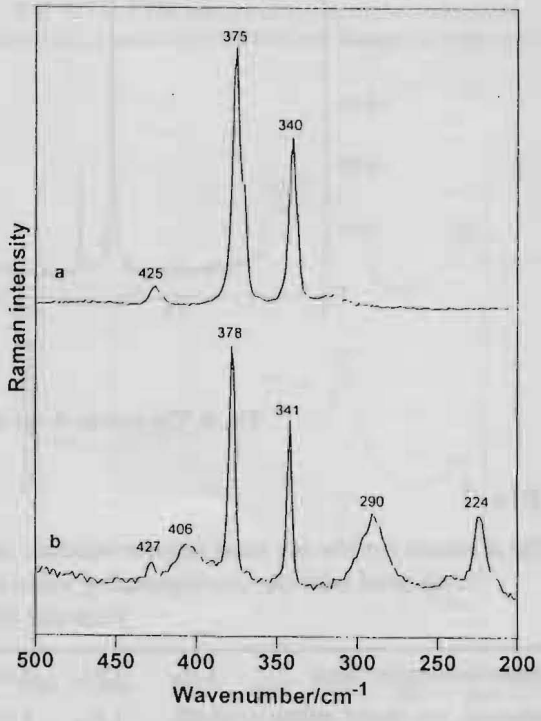

Fig. 8. The Raman spectra of pyrite from Bučim (a) and Sasa (b)

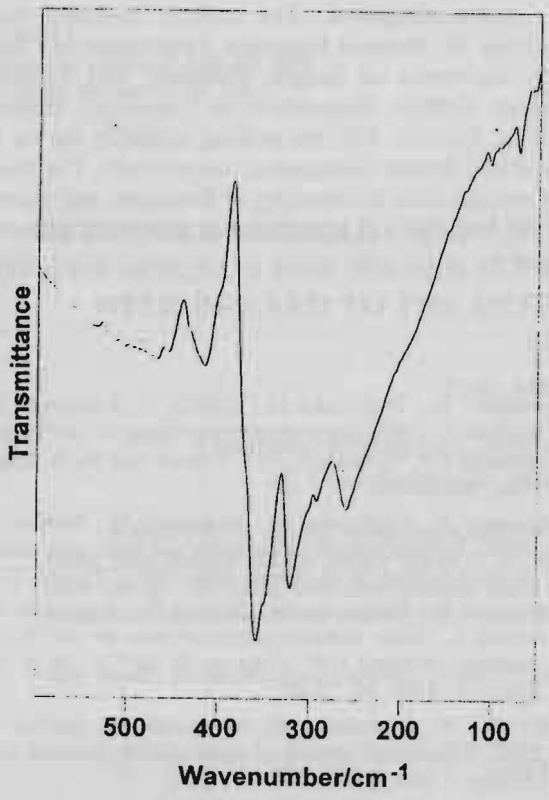

Fig. 9. The FTIR spectrum of chalcopyrite from Zletovo

Chalcopyrite

The infrared spectrum of the studied chalcopyrite sample from Zletovo (375, 357, 320 and 257 cm^{-1}) (see Fig. 9) is practically identical with the published infrared spectrum of mineral chalcopyrite (374, 361, 323 and 264 cm^{-1}) (Soong and Farmer, 1978). The additional very weak band observed by Soong and Farmer at 397 cm^{-1} in our spectrum appears as shoulder at around 400 cm^{-1}. The observed weak bands above 400 cm^{-1} indicate the presence of some impurities in the studied sample (see further discussion concerning the Raman spectrum).

The chalcopyrite sample from Zletovo has also been studied by Raman spectroscopy. The frequencies of the three bands in our Raman spectrum (373, 338 and 287 cm^{-1}) (see Fig. 10) are close to those (378, 352 and 293 cm^{-1}) found in the literature (Mernagh and Trudu, 1993). The forth, weak band recorded by Mernagh and Trudu at 322 cm^{-1}, has not yet been found in our spectra; it is probably overlapped by the rather high spectral background. It should be mentioned that the bands at 373 and 338 cm^{-1} in the spectrum of the studied sample have very similar frequencies with the already discussed bands in the Raman spectrum of pyrite (377 and 342 cm^{-1}) (Fig. 8). Since the intensity of the two latter bands is rather strong, we may consider that chalcopyrite weak bands at 373 and 338 cm^{-1} are overlapped with the pyrite strong bands at 377 and 342 cm^{-1}. This indicates that pyrite impurities are present in the studied specimen. The presence of the non-characteristic band for the chalcopyrite in the spectrum of the studied by us specimen at 468 cm^{-1} is an additional indication about the presence of the impurities in the studied sample. Having in mind the previously discussed indications about the presence of impurities of chalcopyrite in the studied pyrite samples, it is obvious that complete separation of these two minerals is very often practically impossible.

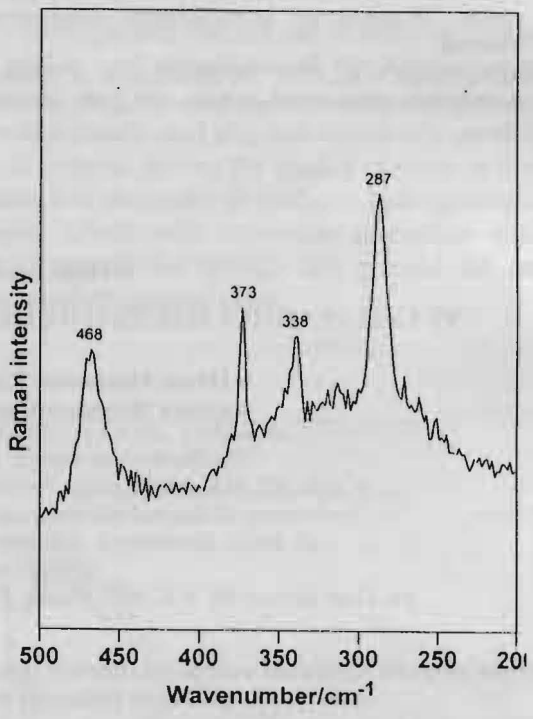

Fig. 10. The Raman spectrum of chalcopyrite from Zletovo

CONCLUSION

The infrared and Raman spectra as well as the powder X-ray diffraction patterns, enable a rapid check on the purity of sulfide mineral galena, sphalerite (wurtzite), pyrite and chalcopyrite, and give an unambiguous opportunity for their identification.

During this process, some of the problems that could arise are: (i) the presence of certain

quantity of impurities in the studied samples, (ii) the decomposition of the sample during the process of spectrum recording, (iii) the lack of the literature data for comparison, and others.

Differences in the sensitivity to impurities between the vibrational and structural techniques justify their simultaneous application, showing that they are complementary rather than competitive.

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Резиме

МИНЕРАЛИ ОД МАКЕДОНИЈА

VI. СЕПАРАЦИЈА И ИДЕНТИФИКАЦИЈА НА НЕКОИ СУЛФИДНИ МИНЕРАЛИ

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Клучни зборови: сулфидни минерали; галенит; сфалерит/вурцит; пирит; халкопирит; Македонија; Фуриеова трансформна (FTIR) и раманска спектроскопија, рендгенска дифракција, спрашени примероци

Македонија располага со богати рудни наоѓалишта од кои најексплоатирани се сулфидните минерали. Некои од овие минерали се појавуваат во природата како добро оформени монокристални примероци, но често се случува тие да бидат придружени и со присуство на други минерални форми. Во овој труд се дискутирани тешкотиите што се јавуваат при процесот на селекција, сепарација, прочистување, идентификација и карактеризација на некои сулфидни минерали (галенит, PbS; сфалерит/вурцит, (Zn,Fe)S; пирит, FeS_2; халкопирит, $CuFeS_2$) од разни локалитети (Саса, Бучим, Злстово, Тораница) во Македонија. Идентификацијата е заснована на споредба на нашите резултати (добиени со помош на инфрацрвена и раманска вибрациона спектроскопија и рендгенска дифракција на спрашени примероци) со соодветните литературни податоци за аналогните минерални примероци по потекло од разни места во светот.